# 1. Introduction

The first observation of ferroelectricity was made in 1921 when Valasek [1] discovered that the polarization in Rochelle salt ($NaKC_2H_4O_6.4H_2O$) gets reversed on application of an electric field. The phenomenon was first referred to as "Seignette-electricity", in reverence of the discovery of the Rochelle salt. However, the phenomenon was not studied broadly until simpler phosphates and arsenates, which exhibited the behaviour, were developed in 1935-1938 [2]. In view of an established analogy between ferromagnetism and ferroelectricity, the term "ferroelectricity" came into general use in early 1940s. Ferroelectric behaviour arises as a result of competition between long-range forces of ionic charges in the material, which acts to stabilize the ferroelectric phase, and short-range, repulsive forces, which favour non ferroelectric symmetric structure [3-5]. On the basis of physical and mechanical properties, ferroelectric materials are broadly categorized into two groups; (i) soft ferroelectrics (potassium dihydrogen phosphate (KDP)-type), and (ii) hard ferroelectrics (barium titanate ($BaTiO_3$) –type). The phase transition in soft (H-bonded) ferroelectrics is of order–disorder type [6] while for the hard ones (i.e., $BaTiO_3$), it is of displacive-type [2, 7].

The members belonging to the family of oxygen octahedra with one or more component oxides play a significant role in ferroelectrics**.** All the materials of this structure have $BO_6$ oxygen octahedral**,** even though they have different crystal structures, electrical and mechanical properties, transition temperature ($T_c$) and polarization [8]**.** The family of oxygen octahedral ferroelectrics has four basic structures namely:

1. Perovskite type
2. Tungsten –Bronze type
3. Spinel Structure (Layered oxides)
4. Pyrochlore type

Among all the ferroelectrics materials, perovskites are the most widely and extensively studied family. The general formula of a perfect perovskite structure is $ABO_3$ where A is a large cation (mono to trivalent) and B is a small cation (a transition metal ion with oxidation number 4 - 6). The A ions occupy the corners of the cube which is 12

coordinated, the B ions sit on the body center positions inside an oxygen octahedron, and $O^{2-}$ ions are at the face center positions The first perovskite discovered was $BaTiO_3$ (barium titanate) [9] in the year 1945. After that, a large number of ferroelectric perovskite doped with different ions at the A and B sites (in search of new materials for device applications) have been discovered. Some of the simple and complex oxides, derived from perovskite structure, are extensively studied for their greater structural stability required for devices [2, 10]. In the quest of discovering new simple and complex oxides, many materials of rare earth ions comprising ternary calcium oxa-metallate family have been studied [11].

Recently, cation-deficient hexagonal (perovskite based) materials have attracted much attention due to their low dielectric losses, relatively high permittivity and small temperature coefficient of resonant frequency for applications in microwave technologies. Among these hexagonal perovskite, some compounds with a general formula $A_nB_{n-\delta}O_{3n-x}$ ($\delta \geq 1$, $x \geq 0$) are prepared by varying the ratio of cubic (c) and hexagonal (h) stacking of ($AO_3$) layers with B-cation occupying octahedral cavities. When the cationic ratio of A to B is 3:2 (i.e., $n = 3$, $\delta = 2$), one of every three B-sites remain unoccupied and different structures can be formed depending on the composition and extent of anion deficiency [12]. For example, with $x = 0$ two polytypes can be adopted; (a) the $Ba_5Nb_4O_{15}$- type ceramics, where the ($AO_3$) layers are hexagonal close packed and an empty octahedron is situated between face-sharing octahedra [13] and (b) the 9R type structure, where the stacking sequence is $(hhc)_3$ and a vacant octahedral cavity is located between corner-sharing octahedra. The ordered distribution of cation vacancies reduce the repulsion between B-site cations in face sharing octahedra, and hence stabilize the crystal structure [14]. When $x = 1$ (e.g.; $A_3B_2O_8$), the palmierite structure is derived from that of the 9R polytypes.

Brixner and Flournoy [11] studied the effect of fluorescent emission of $Nd^{3+}$, $Sm^{3+}$, $Eu^{3+}$, $Tb^{3+}$ and $Dy^{3+}$ in $Ca_3(VO_4)_2$ (calcium orthovanadate) host as a function of rare earth concentrations and reported the optimum concentration for maximum fluorescence. Grzechnik and McMillan, in 1997 presented the Raman spectrum of barium orthovanadate, $Ba_3(VO_4)_2$, at ambient conditions [15]. Grzechnik et al [16], in 2002 further reported the crystal structure of a new polymorph of calcium orthovanadate $Ca_3(VO_4)_2$, prepared at 11 GPa and 1373 K. Umemura et al [17] reported the effect of low temperature sintering on the microwave dielectric properties of $Ba_3(VO_4)_2$ ceramic.

Merkle et al [18] reported a three-level laser oscillator operation in a material Mn:$Ba_3(VO_4)_2$ at room temperature under pulsed 592 nm excitation. Buijsse and others [19] studied the lowest $^3A_2$ state of manganese-doped $Ba_3(VO_4)_2$ using Electron-spin-echo spectroscopy. Khatri et al [20] reported the structural and electrical properties of barium orthovanadate ceramic, prepared by a standard solid-state reaction route. The same research group has also reported the structural and electrical properties of two other compounds of the same orthovanadate family; $Sr_3V_2O_8$ and $Ca_3V_2O_8$ [21, 22]. Parhi et al [23] reported the synthesis of metal orthovanadates $M_3V_2O_8$ (M= Ca, Sr and Ba) by a solid-state metathesis approach initiated by microwave energy. Shim et al [24] reported the characterization of $Sr_3V_2O_8$ nanoparticles, prepared using MAS (microwave-assisted solvothermal) route followed by further heat treatment. Vanderah et al [25] reported the crystal chemistry and phase equilibria in BaO rich BaO-$Nb_2O_5$ binary system and alumina modified BaO-$Nb_2O_5$ systems. The structural studies on the compounds of these systems found to be consistent with previously suggested structural models. Gonzalez et al [26] proposed a new structural model for barium orthoniobate ($Ba_3Nb_2O_8$) using high-resolution electron microscopy (HREM) study. Brown Holden and others [27] studied the Raman scattering spectra of two cation-defficient perovskite-like oxides; $Ba_3MoNbO_{8.5}$ and $Ba_7Nb_4MoO_{20}$ and proposed the distribution of octahedral and tetrahedral in hexagonal perovskite-like oxides with the general formula $A_nB_{n-\delta}O_{3n-x}$ ($\delta \geq 1$, $x \geq 0$). Bezak et al [28] reported the polymorphic phase transition in $Ba_4Nb_2O_9$ using thermal analyses, high-temperature transmission electron microscopy and x-ray powder diffractometry. Manolikas and others [29] reported the low temperature phases in lead orthovanadate $Pb_3(VO_4)_2$ based on electron diffraction and transmission electron microscopy study. Kuok and others [30] studied the low-temperature phase transition in lead orthovanadate using Raman spectroscopy. Dudnik et al [31] reported the structural peculiarities common to some pure ferroelastics. The study revealed that 68 perovskite type compounds attributed to ferroelastics and categorised into 15 structural families, which also includes the palmierites. Kiat and others [32] reported the three phases of lead orthovanadate based on their Neutron and X-ray powder diffraction study. Yan et al [33] reported the fabrication of ferroelectric-gate field effect transistors (FeFETs) with $SrBi_2Ta_2O_9$ (SBT) ferroelectric layers, prepared using the metal-organic chemical vapour deposition (MOCVD) technique.

The present study mainly focused on synthesis and characterization of orthometallates of alkaline earth metals with a general formula of $A_3 (BO_4)_2$ (A= divalent metals such as Pb, Sr and Ba and B = pentavalent metals such as V, Nb and Ta), prepared by a solid-state reaction technique. The substitution of different divalent metal ions at the A-site and pentavalent metal ions at the B-site is carried out to determine the suitability of the substituting elements to tailor various physical properties (structural, microstructural, dielectric, pyroelectric, ferroelectric and electrical) of the materials for the better understanding. Secondly, lead-based ceramics exhibits compositional fluctuations due to evaporation of PbO. As a result, the mechanical and electrical properties of the materials are greatly affected. At the same time there is a possibility of environmental pollution that might arise due to incorrect approach during fabrication of the lead-based ceramics. In view of the importance of the lead-free materials, the present work also focused on looking into the change observed in different parameters as we move from lead-based compounds to their non-lead counterparts in a particular series.

## 2. Objectives of the present work

The objectives of the present work have been defined on the basis of the existing literatures and challenges in the field of ferroelectrics with emphasis on the compounds of orthometallate family.

- ✓ Synthesis of the compounds using a high-temperature soli-state reaction technique.
- ✓ Structural and microstructural studies of the compounds to study the relation between crystal structure and particle size of the compounds.
- ✓ To study the dielectric properties in a wide range of temperature and frequency.
- ✓ To study the electric polarization of the compounds to have additional evidences for their ferroelectric properties.
- ✓ To study the pyroelectric properties of the compounds in support of their dielectric behavior.
- ✓ To analyze the electrical properties of the compounds by complex impedance spectroscopy (CIS) technique to explore the structure- property relationship.

- ✓ Studies of the dc and ac electrical conductivity as a function of frequency and temperature for better understanding of the conduction process present in the compounds.

## 3. Materials under present study

In the present study, the following ferroelectric orthometallates have been studied.

$A_3B_2O_8$ Or $A_3(BO_4)_2$ with A = Pb, Sr and Ba; B = V, Nb and Ta

## 4. Outline of the thesis

The thesis has been divided into seven chapters as described below.

- **Chapter 1** describes a brief introduction of ferroelectrics with a specific mention of ferroelectric orthometallates. Summarized reviews of work done on synthesis and different properties of ferroelectric orthometallates and related compounds have been presented to have an overview of the conceptual, theoretical and material aspects of these compounds. In the light of literature survey, the main objectives of the present work have been formulated.
- **Chapter 2** describes the sample preparation technique with emphasis on the high-temperature solid-state reaction. Some common analysis methods are surveyed and a brief description of the instruments and setups used in the present investigation is given.
- **Chapter 3** reports the structural and microstructural characterization of the compounds using X-ray diffraction and scanning electron microscopy (SEM) techniques respectively.
- **Chapter 4** describes the study of dielectric and ferroelectric properties of the compounds.
- **Chapter 5** deals with an extensive study of complex impedance spectroscopy of the compounds.
- **Chapter 6** describes of the electrical conductivity of the studied compounds.
- **Chapter 7** gives a brief summary, conclusion and future scope of the work.

## 5. Sample preparation

The polycrystalline samples of $A_3B_2O_8$ (A = Pb, Sr and Ba and B = V, Nb and Ta) were prepared using high-purity oxides/carbonates by a high-temperature solid-state reaction route as per the chemical equation:

$3(ACO_3) + B_2O_5 \rightarrow A_3B_2O_8 + 3CO_2$, where A = Sr and Ba and B = V, Nb and Ta.

For lead-based compounds the following chemical equation was used.

$3PbO + B_2O_5 \rightarrow Pb_3B_2O_8$, where B was the same as above.

For the synthesis of the above compounds, high-purity AR (Analytical Reagent) grade precursors; $Ba_2CO_3$ (99.9 % M/s Sarabhai M. Chemicals Pvt. Ltd., India), $Sr_2CO_3$, PbO (99%, M/s LOBA Chemie Pvt. Ltd., India), $V_2O_5$, $Nb_2O_5$ and $Ta_2O_5$ (99.9%, M/s LOBA Chemie Pvt. Ltd., India) were taken in a proper stoichiometry. These ingredients were first mixed mechanically in an agate-mortar and pestle for an hour. This was followed by wet grinding (in methanol) for another hour to get a homogeneous mixtures of the constituents. The mixed powders of the compounds were finally calcined at temperatures ranging from 750$^o$C - 1425$^o$C (as decided by repeated firing/mixing) in alumina/platinum crucibles for 4 h in air atmosphere. The calcination temperatures of various compounds (as decided by repeated firing/mixing) were recorded in Table 2.1 of Chapter 2. The formation and quality of the desired compounds were checked from the x-ray diffraction (XRD) pattern of the materials, recorded at room temperature using a Philips X'Pert Pro PANalytical powder diffractometer (Model PW 3040/60, DISIR, Rajgangpur, India) with $CuK_\alpha$ radiation ( $\lambda$ = 1.5405 Á) in a wide range of Bragg angle $\theta$ ($0 \leq 2\theta \leq 60$) at a scanning rate of $2^0$/min. The calcined powder of the compounds were cold pressed into cylindrical pellets (10-12 mm diameter and 1-2 mm thickness) using polyvinyl alcohol (PVA) as the binder and applying an isostatic pressure of $4\times10^6$ N/m$^2$. PVA was used as a binder to reduce the brittleness of the pellets. The pellets were then sintered in air atmosphere at optimized temperatures ranging from 780$^o$C - 1480$^o$C for 6 h followed by furnace cooling. The optimized sintering temperatures of various compounds were recorded in Table 2.1. The calcination and sintering of some compounds (having the said temperatures greater than1400$^o$C) were carried out in a platinum crucible. The crystal structure and microstructures of the prepared compounds were studied by X-ray diffraction technique (XRD) and scanning electron microscopy

(SEM) respectively. The flat and parallel surfaces of the sintered pellet were polished with fine emery paper and electroded with air-drying conducting silver paste. The pellets were dried at 150$^{o}$C for 8 h to remove moisture (if any) before taking electrical measurements. The dielectric and other related parameters were measured as a function of temperature (30-500$^{o}$C) and frequency (1 kHz – 1 MHz) using a computer-controlled phase sensitive meter (PSM LCR 4NL, Model: 1735, UK), a laboratory-designed sample holder and a small vertical pit furnace. An input signal of constant voltage amplitude ~ 1V was applied across the sample for the measurement. The polarization (hysteresis loop) of the poled sample (electric field= 10 kV/cm, time= 8 h) was obtained at different temperatures using a workstation of hysteresis loop tracer (M/S Marine India, New Delhi). The pyroelectric current of the pellet sample was measured at different temperature (30- 480$^{o}$C) by an electrometer (KEITHLEY INSTRUMENTS INC., MODEL 6517B) at the heating rate of nearly 2$^{o}$C/min. A constant voltage was applied across the sample to measure the dc conductivity using the same electrometer.

## 6. Structural studies

The x-ray diffraction patterns show a number of sharp peaks, different from those of the ingredients. The patterns also reveal better homogeneity and crystallization of the materials, and thus confirm the formation of single-phase compounds without any significant trace of pyrochlore and any other phases. The well-resolved sharp peaks in the XRD patterns indicate the materials are highly crystallized [34, 35]. All the peaks of most of the patterns could be assigned to the hexagonal phase, and some to trigonal phase. The lattice parameters of the selected unit cell were refined using the least-squares sub-routine of the standard computer program package "POWD mult" [36]. The values of a, b and c have been refined using least-squares fit of the positions/interplanar spacing (d) of the peaks so that $\Sigma\Delta d = \Sigma (d_{obs} - d_{cal})$ was found to be minimum. This shows a good agreement between the observed (obs) and calculated (cal) values of interplanar spacing, and hence confirms the correctness of the chosen crystal system and unit cell parameters. Further, the scattered crystallite or particle size (p) of the compounds was calculated using the broadening of some widely spread (over Bragg angles) strong and medium reflections in the Scherrer's equation: $p_{hkl} = \frac{K\lambda}{\beta_{1/2} Cos\theta_{hkl}}$, where K (constant) = 0.89, $\lambda$=1.5405$^{0}$A and $\beta_{1/2}$= full width at half maximum (in radians) [37]. The

contributions of strain and other effects in the broadening of XRD peaks and crystallite size calculation have been ignored due to the use of powder sample [38].

The surface morphology of the investigated compounds was recorded at room temperature using scanning electron microscope (SEM) technique. The microstructures of the sintered pellets show that the grain growth process is more or less completed during sintering and no secondary re-crystallization has been taken place. The micrographs exhibit a well-defined and homogeneous morphology for the samples [39]. In spite of sintering at optimized high- temperature, some voids of irregular shape and dimension are still observed in the micrographs of some of the studied compounds. Most of the grains have dimension in the range of ~2-6μm.

## 7. Dielectric Studies

The basic study on electrical properties of materials reveals that their dielectric parameters ($\varepsilon_r$ and tanδ) are not only dependent on their geometry and temperature, but also on the frequency of applied electric field [40]. The relative permittivity ($\varepsilon_r$) and loss tangent (tanδ) of all the compounds were obtained both as a function of frequency (1 kHz – 1 MHz) and temperature (from room temperature to 500$^oC$) using a computer-controlled phase sensitive meter (PSM LCR 4NL, Model: 1735, UK), a laboratory-designed sample holder and a small vertical pit furnace. An input signal of constant voltage amplitude ~ 1V was applied across the sample for the measurement. These dielectric parameters ($\varepsilon_r$ and tanδ) were found to decrease on increasing frequency, which is a general feature of dielectric materials [41]. At higher frequencies these parameters become almost frequency independent. From detailed analysis, it was observed that most of the studied compounds (except $Pb_3V_2O_8$ & $Pb_3Nb_2O_8$) of this orthometallate family were expected to have ferroelectric to paraelectric phase transition at very high temperature. Three samples ($Sr_3V_2O_8$, $Sr_3Nb_2O_8$ & $Ba_3Nb_2O_8$) show dielectric anomaly, i.e. ferroelectric to paraelectric phase transition of diffused type in the studied temperature range. The broadening of permittivity peaks with increasing frequencies along with the limiting values of $\gamma$ $(1 < \gamma < 2)$ confirms the presence of diffuse phase transition in these materials [42]. Two samples ($Pb_3V_2O_8$ & $Pb_3Nb_2O_8$) have ferroelectric to paraelectric phase transition below room temperature [29]. The study further reveals that *tanδ* decreases with increase in frequency of the applied alternating electric field. This is because of the hopping frequency of charge carriers fails

to follow the altering field after certain frequency. Due to enhanced hopping of thermally energized electrons tanδ increases with the increase in temperature. The rate of increase in tanδ in the materials, in the low and medium temperature regions, is slow, whereas at higher temperatures the increase is relatively sharp. This sharp increase in tanδ at higher temperatures may be due to a) scattering of thermally activated charge carriers, b) some inherent defects in the sample and c) creation of oxygen vacancies during sample preparation [43].

The temperature dependence of hysteresis loops of the poled samples was obtained using hysteresis loop tracer of M/S Marine India, New Delhi. The nature of the loop at room temperature along with the decrease in remnant polarization, coercive field and area of the loop with temperature, confirms the existence of ferroelectric properties in most of the materials [44]. The absence of hysteresis loop in $Pb_3V_2O_8$ & $Pb_3Nb_2O_8$ at room temperature supports their dielectric study.

Ferroelectric materials, a sub-group of pyroelectric materials, exhibit temperature dependent spontaneous electric polarization, i.e. polarization that changes with temperature [45]. Pyroelectric current (*I*), developed on the surface of the material sample, can be expressed as per the relation: $I = \Gamma A \frac{d\theta}{dt}$ where A is the area of the sample, $\Gamma$ is the pyroelectric coefficient and $\frac{d\theta}{dt}$ denotes the time rate of change of temperature of the material. Most of the studied compounds, except two ($Pb_3V_2O_8$ & $Pb_3Nb_2O_8$), show pyroelectricity that supports their dielectric response. The relatively high pyroelectric coefficient of the samples reflects the good stoichiometry.

## 8. Complex impedance and modulus spectroscopy

Study of electrical properties is an important part of materials characterization to verify the suitability of the materials for device application. Complex impedance spectroscopy (CIS) is a flexible tool for the simultaneous dielectric and electrical characterization. One of the most attractive aspects of CIS as a tool for studying the electrical properties of materials is the direct relation between the behaviors of the system and is an ideal model of electrical circuit consisting of discrete electrical components [46, 47]. The polycrystalline materials show a variety of frequency

dependent effects associated with heterogeneities such as grain, grain boundary etc. For complete characterization of the materials, variable frequency methods have extensively been used. The advantage of frequency dependent measurements is that the contributions of the bulk (grains), grain boundaries electrode material interface effects can easily be separated if the time constants are different enough to allow separation [48]. In our present study, we have employed this technique to study complex impedance formalism, complex electric modulus formalism and relaxation process of the materials under investigation. Complex impedance spectra indicate the possible contribution of the bulk and grain boundaries at higher temperatures, and also the temperature dependent relaxation phenomena. The appearance of depressed semicircles also supports the non-Debye type relaxation in these samples. In most of the non-lead materials (except $Sr_3V_2O_8$), the electrical processes arise basically due to the contribution from bulk material. However, in the lead based compounds such as $Pb_3V_2O_8$, $Pb_3Nb_2O_8$, $Pb_3Ta_2O_8$ and non-lead $Sr_3V_2O_8$ there is an additional contribution from grain boundaries along with the bulk effect. The bulk resistance ($R_b$) and grain boundary resistance ($R_{gb}$) were calculated by theoretically fitted data by using commercially available software ZSIMP WIN version 2. It is found that both $R_b$ and $R_{gb}$ of all the compounds decrease with rise in temperature signifying NTCR behavior of the materials [49]. The semi- circles in the impedance spectrum have a characteristic peak occurring at a unique frequency usually referred as resonance frequency ($f_r$) ($\omega_r = 2\pi f_r$). It can be expressed as $\omega_r RC = \omega_r\tau = 1$ and thus $f_r = 1/ 2\pi RC$, where $\tau$ is the relaxation time. The relaxation time due to bulk effect ($\tau$) has been calculated using the equation $\omega_r\tau = 1$ or, $\tau = 1 / 2\pi f_r$. The activation energy ($E_a$) of the compounds under study was calculated from the Arrhenius relation: $\tau = \tau_0 \exp(-E_a/kT)$ where $\tau_0$ is the pre exponential factor, k is Boltzmann constant and T is the absolute temperature. The value of activation energy is calculated from the slope of $\ln\tau$ vs. 1000/T. The activation energy for all the compounds is small, lying in the range (0.44 eV - 1.01 eV) which represents localized hopping of charge carriers [50].

For all the compounds, it is observed that the value of Z' decreases with rise in both temperature and frequency [51, 52]. The value of Z' decreases with increase in temperature in the low-frequency region showing negative temperature coefficient of resistance (NTCR) behavior, and they merge in the high-frequency region irrespective of change in temperature. This nature may be due to the release of space charge [53]. The decrease of Z' with temperature indicates the presence of dielectric relaxation in the

samples. The frequency dependence of Z" plots reveal that the peaks ($Z"_{Max}$) shift towards higher frequency on increasing temperature due to decrease in the bulk resistance [54, 55].

Electrical response of a sample can also be analyzed using complex modulus formalism. Complex impedance spectrum relies on the largest resistance whereas complex modulus spectrum highlights on the smallest capacitance. In complex modulus formalism, we have studied Nyquist plots (M' vs. M"), the frequency dependence of M' and M", where $M' = \omega C_0 Z"$ and $M" = \omega C_0 Z'$. Here $\omega$ (= $2\pi f$) is the angular frequency, $C_0$ is the capacitance of the cell in air/vacuum = $\varepsilon_0 (A/t)$ and $\varepsilon_0$ is the permittivity of the free space, A is the area of the electroded surface of the sample and t the thickness of the sample. The real and the imaginary part of electric modulus are indicative of the stiffness and energy loss of the materials under electric field respectively. This formalism has the advantage to eliminate the contribution of electrode polarization and other interfacial effects in solid electrolytes [36].

It has been observed from the complex electric modulus spectrum (M' vs. M″ plots) of the studied compounds that the curves don't form exact semicircles. They rather possess a shape of depressed semicircles with their centers positioned below the M'-axis. This indicates the spread of relaxation with different time constants, and hence, suggests the presence of non-Debye type of relaxation in the materials.

It has been observed from the above figures that the value of M' approaches zero on lowering frequency with monotonic dispersion, whereas with rise in frequency the values of M' coincide. The monotonic dispersion with rise in frequency may be due to presence of conduction phenomenon and short range mobility of charge carriers.

The frequency dependence of M" at some selected temperatures reveal that the value of M" is nearly zero at lower frequencies, increases to a maximum and then decreases. The frequency where M" reaches a maximum is called the relaxation frequency. The plot also shows that $M''_{max}$ peak shifts towards higher frequency side on increasing temperature. The temperature dependence of asymmetric broadening of the peak confirms the spread of relaxation with different time constants, and hence, confirms the Existence of non- Debye type relaxation in the materials [53, 55].

## 9. Electrical conductivity studies

The study of electrical conductivity is much significant in case of dielectric/ferroelectric materials because most of the physical properties (such as dielectric, mechanical or optical, etc.) are related to their response to electric signal/perturbation.

The ac electrical conductivity ($\sigma_{ac}$) was calculated using the dielectric data using an empirical relation; $\sigma_{ac} = \omega\varepsilon_r\varepsilon_0 \tan\delta$, where $\varepsilon_0$ is the absolute permittivity of free space, and $\omega$ is angular frequency [41]. The occurrences of different slopes in different regions of the temperature dependent plots of $\sigma_{ac}$ indicate the presence of multiple conduction mechanisms in the materials with different values of activation energy. In the low-temperature region, the activation energy is low and the conductivity is strongly dependent on frequency, while at higher frequencies the activation energy is high, which well agrees with hopping mechanism. The ac conductivity follows the Arrhenius relation $\sigma = \sigma_0 \exp(-E_a/k_BT)$ and the activation energy $E_a$ is calculated from the slope of the linear portion of the plot $\sigma_{ac}$ versus $10^3/T$ graph). The activation energies of the compounds lie in the range of 0.25 eV to 1.68 eV for all the studied compounds.

It was found that $\sigma_{ac}$ decreases on decreasing frequency, and becomes independent of frequency after a certain value. Extrapolation of this part towards lower frequency will give $\sigma_{dc}$ [56]. It was also found that the slope changes at a particular frequency. This frequency shifts towards higher side with rise in temperature, known as hopping frequency/polaron frequency ($\omega_p$). The fitting of experimental data (frequency dependent of ac conductivity) was carried out using some theoretical models. It has been observed from the variation of fitting parameters A and n with temperature that, for all samples the value of the parameter n decreases with rise in temperature attains a first minimum and subsequently increases. The pre-exponential factor A, shows a trend opposite to that of n, i.e., it attains a maximum where n is minimum [57].

The study of current density (J) versus electric field (E) characteristics of ferroelectric ceramics is a useful characterization technique to understand the conduction mechanism in the sample. The current density increases with rise in temperature showing the NTCR behaviour of the samples [54]. The value of the dc conductivity ($\sigma_{dc}$) determined from slope of J~E characteristics plots can be considered as the true value of

conductivity of the samples. J~E measurement was completed in electrometer (Keithley Instruments- model 6517B) by applying constant voltage across the sample. The dc conductivity can also be calculated from the impedance spectrum. The nature of the plots and the values of activation energies are consistent, and also are in good agreement with that obtained from J~E characteristics. The dc conductivity also follows the Arrhenius law; $\sigma_{dc} = \sigma_0 \exp(-E_a/k_BT)$. The activation energy $E_a$ is calculated from the slope of the linear portion of the plot ($\sigma_{dc}$ versus 1000/T graph). The J~E plots reveal that these materials allow very small leakage current to pass through them.

## 10. Summary and Conclusion

Based on the experiments performed, the following inferences can be drawn on synthesis, structural, dielectric, polarization, pyroelectric and electrical properties of the studied compounds.

- ✓ All compounds are synthesized by a high-temperature solid-state reaction route. The calcination temperature of these compounds ranges from 750$^o$C to as high as 1450$^o$C. The details of calcination and sintering temperatures were discussed in chapter 2.

- ✓ Most of the studied compounds of this orthometallate family were observed to be of single-phase with hexagonal crystal symmetry at room temperature. Out of the above, two compounds $Ba_3V_2O_8$ and $Sr_3V_2O_8$ have trigonal crystal symmetry. The well-resolved sharp peaks in the XRD pattern indicate the materials are highly crystallized. The study also suggests, the solid-state reaction technique is suitable for the growth of $A_3B_2O_8$ (A= Pb, Sr, Ba and B= V, Nb, Ta) crystallites with development of some high intensity peaks from different planes in the preferred orientations.

- ✓ The SEM micrographs exhibit a well-defined and homogeneous morphology for the samples with minimum voids/pores.

- ✓ Most of the studied compounds of this orthometallate family were expected to have ferroelectric to paraelectric phase transition at very high temperature (>500$^o$C). Three samples ($Sr_3V_2O_8$, $Sr_3Nb_2O_8$ & $Ba_3Nb_2O_8$) show dielectric anomaly, i.e. ferroelectric to paraelectric phase transition of diffused type. Two

samples ($Pb_3V_2O_8$ & $Pb_3Nb_2O_8$) have ferroelectric to paraelectric phase transition below room temperature. The variation of tanδ with temperature exhibits an increasing trend for all compounds. The values of dielectric parameters show a decreasing trend as we move from lead based compound to corresponding non-lead species in a particular series.

- ✓ The values of diffusivity (γ) within range ($1 < \gamma < 2$), clearly suggests the presence of diffuse phase transition in compounds $Sr_3V_2O_8$, $Sr_3Nb_2O_8$ & $Ba_3Nb_2O_8$.

- ✓ The nature of the hysteresis loop at room temperature along with the decrease in remnant polarization, coercive field and area of the loop with temperature, confirms the existence of ferroelectric properties in the material. Most of the studied compounds, except two ($Pb_3V_2O_8$ & $Pb_3Nb_2O_8$), show polarization, i.e. hysteresis loop below transition temperature confirming their ferroelectric properties.

- ✓ Most of the studied compounds, except two ($Pb_3V_2O_8$ & $Pb_3Nb_2O_8$), show pyroelectricity that supports their dielectric response. The relatively high voltage responsivity and detectivity of these materials are expected to be useful for pyroelectric detector with fairly high efficiency well above room temperature.

- ✓ Complex impedance spectroscopy, in terms of a simultaneous analysis of the complex impedance and electric modulus is used to investigate the electrical behaviour of these ceramics. The use of the function $Z^*$ and $Y^*$ is suitable for the resistive and/or capacitive analyses when the long range conductivity dominates while the $M^*$ and $\varepsilon^*$ functions are appropriate when localized relaxation dominates.

- ✓ Complex impedance spectra indicate the possible contribution of the bulk and grain boundaries at higher temperatures, and also the temperature dependent relaxation phenomena. The appearance of depressed semicircles also supports the non-Debye type relaxation in these samples.

- ✓ In most of the non-lead materials (except $Sr_3V_2O_8$), the electrical processes arise basically due to the contribution from bulk material. However, in the lead based compounds such as $Pb_3V_2O_8$, $Pb_3Nb_2O_8$, $Pb_3Ta_2O_8$ and non-lead $Sr_3V_2O_8$ there is

an additional contribution from grain boundaries along with the bulk effect. The decrease in bulk resistance and grain boundary resistance (wherever exists) with increasing temperature suggests the NTCR behaviour of the samples.

- ✓ Both imaginary impedance and modulus exhibits temperature dependent electrical relaxation phenomena at higher temperatures. Relaxation processes are due to short range mobility of charge carriers of similar type. Distributed relaxation time suggests the dielectric relaxation in all these materials is of polydispersive non-Debye type.

- ✓ Conductivity behaviour with respect to frequency obeyed Jonscher's power law and the non linear fitting showed that the value of n remained equal or less than unity in most of the compounds.

- ✓ The temperature dependence of ac conductivity data showed that the hopping of charge carriers between the trap sites is responsible for high conduction in these materials and thus ensure different activation energies in different temperature regions.

- ✓ The study of dc conductivity confirms the NTCR behaviour of these samples. The nature of the temperature dependence of $\sigma_{dc}$ plots for all the studied materials follows Arrhenius relation.

- ✓ The smaller values of both dc and ac activation energies suggests that these materials can be activated on applying a smaller energy.

## 11. Possible device applications

- ✓ The low relative permittivity and low tangent loss of $Ba_3V_2O_8$ and $Sr_3V_2O_8$, make them potential candidates for microwave applications.

- ✓ The relatively high voltage responsivity and detectivity of these materials (with suitable modifications) are expected to be useful for pyroelectric detector with fairly high efficiency well above room temperature.

## 12. Scope of future studies

- ✓ Investigation of the optical properties of all the studied compounds using various spectroscopies to understand the structure and symmetry of these compounds with an insight into their different physical properties.
- ✓ Examination of size effect of different ions at the A-site and/or B-site of these studied samples on various (structural, mechanical, optical, electrical etc.) properties.
- ✓ Exploitation of small relative permittivity and very small loss in these metal orthovanadates and for possible microwave applications, with suitable modifications.
- ✓ Exploitation of high pyroelectric coefficient and relatively high voltage responsivity and detectivity in some of these orthometallates (with suitable modifications) useful for detector applications.

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## List of publications in International Journals related to Thesis


**1.** **Biswajit Pati**, B. C. Sutar, B. N. Parida, P. R. Das, R. N. P. Choudhary, "Dielectric and impedance spectroscopy of barium orthovanadate ceramics", J. Mater. Sci: Mater. Electron., **24(5)** (2013) 1608-1616.

2. **Biswajit Pati**, R. N. P. Choudhary, P. R. Das, B. N. Parida, R. Padhee, "Dielectric and impedance spectroscopy of barium orthoniobate ceramic", J. Electronic Materials, **42** (2013) 1225-1237.

3. **Biswajit Pati**, R. N. P. Choudhary, P. R. Das, "Phase transition and electrical properties of strontium orthovanadate," J. Alloys & Compd., **579** (2013) 218-226.

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7. **Biswajit Pati**, R. N. P. Choudhary, P. R. Das, B. N. Parida, R. Padhee, "Dielectric and pyroelectric properties of highly crystallized lead-free ferroelectric $Ba_3V_2O_8$", Physica B (***Under review***)

## List of other publications in International Journals

1. R. N. P. Choudhary, **Biswajit Pati**, P. R. Das, R. R. Dash, Ankita Paul, "Development of electronic and electrical materials from Indian Ilmenite", J. Electronic Materials. **42**(4) (2013) 769-782

2. R. N. P. Choudhary, **Biswajit Pati**, P. R. Das, R. R. Dash, Subhashree Swain, "Development of electronic materials from industrial waste Red Mud", J. Mater. Sci: Mater. Electron. **25** (2014) 202-225.

3. P. R. Das, **Biswajit Pati**, B. C. Sutar, R. N. P. Choudhary, "Electrical properties of complex tungsten bronze ferroelectrics; $Na_2Pb_2R_2W_2Ti_4Nb_4O_{30}$ (R = Gd, Eu)", Adv. Mater. Letter, **3(1)** (2012) 8-14.

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5. B. C. Sutar, **Biswajit Pati**, B. N. Parida, P. R. Das, R. N. P. Choudhary, "Dielectric and impedance characteristics of $Ba(Bi_{0.5}Nb_{0.5})O_3$ ceramics", J. Mater. Sci: Mater Electron., **24(6)** (2013) 2043-2051.

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7. B. C. Sutar, R. N. P. Choudhary, P. R. Das, **Biswajit Pati**, "Ferroelectric phase transition and conduction mechanism of $Ba(Bi_{0.5}Nb_{0.5})O_3$ ceramics" J. Adv. Sci. Letter, **20** (2014) 857-861.

## Posters/Oral Presentations in National Conferences

1. "Dielectric and impedance spectroscopy of Barium orthoniobate ceramic" in XVII National Seminar on Ferroelectrics and Dielectrics (NSFD) 2012, Institute of Technical Education & Research, Bhubaneswar.

2. "Synthesis and characterization of Barium orthovanadate ceramic" in National seminar on Physics and Technology of Noble Materials, PTNM 2012, Sambalpur University, Sambalpur.

3. "Ferroelectric phase transition and conduction mechanism of $Ba(Bi_{0.5}Nb_{0.5})O_3$ ceramics" in 31$^{st}$ Convention of Orissa Physical Society & National Seminar on Recent Trends in Condensed Matter Physics (RTCMP) 2014, Institute of Technical Education & Research, Bhubaneswar.

4. "Pyroelectric response and conduction mechanism in highly crystallized ferroelectric $Sr_3(VO_4)_2$ ceramic" in National Seminar on Science and Technology of Functional Materials (NSSTFM) 2013, Hi-Tech College of Engineering, Bhubaneswar.